PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for the Preparation of Chlorine, Bromine or Iodine and for the Preparation of Halogenated Hydrocarbons

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the laws of the Netherlands of 30 Carel van Bylandtlaan, The Hague, Holland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the preparation of chlorine, bromine or iodine from the compounds of these halogens with hydrogen. The invention is of particular importance to the preparation of chlorine from hydrogen chloride. The invention also relates to the preparation of halogenated hydrocarbons.

A known technique to prepare halogens from hydrogen halide compounds is to bring the latter compounds, mixed with oxygen or a free oxygen-containing gas, into contact with a catalyst. In the traditional Deacon process copper compounds were used as a catalyst. Compounds of other metals have since also been suggested as catalysts for this oxidation. In general, the conversion percentages in these known processes are appreciably lower than would correspond with the equilibrium. Not until recently were improvements brought about by the application of combinations of compounds of copper, rare earth metals and alkali metals.

It has now been found that in the oxidation of hydrogen chloride, hydrogen bromide or hydrogen iodide in the gaseous phase, ruthenium compounds are very effective catalysts. With these catalysts the equilibrium can be reached at relatively low temperatures.

The invention can be defined as relating to the preparation of chlorine, bromine and/or iodine from the corresponding hydrogen halides, in which a gaseous mixture containing hydrogen halide and oxygen is brought into contact with a catalyst containing at least one ruthenium compound.

A very suitable ruthenium compound is ruthenium trichloride. In the oxidation of hydrogen chloride temperatures between 250 and 500°C may be used. Especially suitable are temperatures between 325 and 400°C, but the process can quite well be carried out above 400°C.

In the process according to the invention atmospheric pressures have proved very satisfactory. A pressure increase results in a shift of the equilibrium towards halogen and water and may therefore be favourable. Although in general the operating pressure will not be outside the range of 1 to 5 atm abs., the reaction may in principle proceed at either higher or lower pressures, for example, between 0.1 and 100 atm abs.

The ruthenium compounds are preferably applied on a carrier. The usual carriers have given good satisfaction. Examples of suitable carriers are silica gel, aluminium oxide, pumice and ceramic materials. The amount of ruthenium in the catalyst is as a rule between 0.1 and 15% by weight, calculated as metal compound on the sum of metal compound and carrier.

The present catalysts may be applied in both fixed beds and fluidized beds.

The oxidation takes place by means of gaseous oxygen. Usually, the gaseous hydrogen halide is mixed with air. Besides air, however, other free oxygen-containing gases as well as pure oxygen may in principle also be used.

The ratio of hydrogen halide to oxygen may certainly be the stoichiometric one. If desired, however, one may depart from the stoichiometric ratio and pass mixtures over the catalyst in which the ratio of hydrogen halide to oxygen is between five times the stoichiometric ratio of one fifth of this ratio.

The catalyst is supported on a carrier in a conventional manner. A very suitable process is one in which the carrier is mixed with such a quantity of a solution of a ruthenium compound in water as can just be absorbed by the carrier material. In this way the catalyst is distributed uniformly over the carrier, while no remaining solution need be separated. The concentration of the solution is chosen such as to obtain the desired ratio of ruthenium to carrier.

The gaseous mixture used as the starting material may also contain one or more hydrocarbons, in which case these hydrocarbons enter into reaction with the halogen formed. In this manner halogen can be added to unsaturated aliphatic hydrocarbons and halogen can be substituted for hydrogen atoms in saturated aliphatic or cycloaliphatic hydrocarbons as well as in aromatic hydrocarbons. In these cases high conversions of hydrogen halide are as a rule attained even at temperatures that are appreciably lower than in the absence of hydrocarbons. Suitable temperatures are frequently between 100 and 300°C.

EXAMPLE

Preparation of the catalyst

As carrier silica was used with the following properties:

surface area	292 m^2/g
pore volume	0.67 ml/g
average pore diameter	91.4 Å
sodium content	0.13 %
iron content	0.11 %

The carrier was dried for two hours at 500°C and subsequently soaked in a solution of ruthenium trichloride. The impregnated carrier was dried at 100°C and finally heated for three hours in an air stream at 250°C.

The concentration of the solution of the ruthenium trichloride was varied in various experiments to obtain catalysts with different ruthenium contents. The ruthenium contents were calculated as per cent by weight of metal on the sum of metal and carrier.

Preparation of chlorine

Hydrogen chloride gas and air were passed over the catalyst at atmospheric pressure, in a stoichiometric ratio and at a rate of 60 litres HCl per kg catalyst and per hour. The percentage of ruthenium in the catalyst and the temperature were varied.

The table below gives the conversion percentages and, for comparison, the equilibria.

TABLE

	Temperature °C		
% Ru	300	325	350
5.00	—	40	56
8.21	44	66	76
12.91	46	67	79
equilibrium	85	82	79.5

WHAT WE CLAIM IS:—

1. A process for the preparation of chlorine, bromine and/or iodine from the corresponding hydrogen halides, in which a gaseous mixture containing hydrogen halide and oxygen is brought into contact with a catalyst containing at least one ruthenium compound.

2. A process as claimed in claim 1, in which the ruthenium compound is ruthenium trichloride.

3. A process as claimed in claim 1 or 2, in which the temperature is between 250 and 500°C.

4. A process as claimed in claim 3, characterized in that the temperature is between 325 and 400°C.

5. A process as claimed in any of the preceding claims, in which a pressure between 0.1 and 100 atmospheres is applied.

6. A process as claimed in claim 5, in which the pressure is between 1 and 5 atmospheres.

7. A process as claimed in any of the preceding claims, in which the ruthenium compound is supported on a carrier.

8. A process as claimed in claim 7, in which the amount of ruthenium in the catalyst is between 0.1 and 15% by weight, calculated as metal compound on the sum of metal compound and carrier.

9. A process as claimed in any of the preceding claims, in which the ratio of hydrogen halide to oxygen is between five times the stoichiometric ratio and one fifth of this ratio.

10. A process as claimed in any of the preceding claims in which the gaseous mixture which is taken as starting material also contains one or more hydrocarbons.

11. A process substantially as described in the Example.

12. A halogen whenever prepared according to any of the preceding claims.

13. A process for the preparation of halogenated hydrocarbons wherein hydrocarbons are reacted with halogen, characterized in that the reaction is performed in a gaseous mixture as claimed in claim 10.

14. A process as claimed in claim 13, characterized in that the temperature is between 100 and 300°C.

15. Halogenated hydrocarbons prepared according to claim 13 or 14.

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